The acid generation potential of iron precipitates and their sludge in Decommissioning with Ecological Engineering

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TABLE OF CONTENTS

1.0 .....Introduction……1

1.1..... Problem Definition……2

1.2 Secondary Fe(III) hydroxides, oxyhydroxides, and oxyhydroxide sulfates ....……3

1.3 Geochemical Modelling…….....7

1.4 Assessing acidification due to precipitate/ sludge formation……...…… ..9

2.0 .....Materials and Methods……..11

2.1.....Sample collection sites……..11

2.2 Water sample collection and storage…… .11

2.3..... Instrumentation and measurement procedure……12

2.4..... Elemental analysis……13

2.5..... Microbiological isolation and enumeration……..13

2.6 Mineralogical analysis…….…… 14

2.7 Tailings pore water…….…….. 14

3.0 .....Results and discussion……..14

3.1..... Microbes in tailings pore water stored and fresh……..18

3.1.1. ...Microbes in bottles stored with precipitate……..18

3.1.2 Microbes in tailings piezometers…….. ..21

3.2 Mineralogical identifications of iron precipitates…….…… .23

3.3 Acidification of surface water samples……29

4.0 .....Conclusion……36

5.0..... References……..…37

LIST OF TABLES

Table 1a: Elemental concentration (mg/L) of water samples collected from South Bay tailing area on September 10, 1996.....15

Table 1b: Elemental concentration (epm) of water samples collected from South Bay tailings area on September 10, 1996 16

Table 1c: Potential pH development in groundwater from tailings on Sept. 10, 1996……..16

Table 2: Hydrolysis reactions of Fe(III) species and the associated protons produced (from Stumm and Morgan, 1996). 4

Table 2a: .....Microbial diversity in 4.6-year stored groundwater from tailings ……19

Table 2b: .....Enumeration of acidophilic and Fe-oxidizing bacteria in 4.6-year groundwater..20

Table 2c: Densities of microbial groups on slides installed in piezometers 22

Table 3: Amount of protons produced by the hydrolysis of the different secondary Fe(III) phases..5

Table 3a: pH values after storage of cirumneutral surface water in Confederation Lake and in Decant Pond on the tailings (Re-measured on April 22, 2003)……. 31

Table 3b: pH values after storage of cirumneutral surface water in Armanda Lake (Fe=1.99 mg/L; SO4= 118.37 mg/L) (Re-measured on April 22, 2003)……..32

Table 3c: pH values after storage of cirumneutral surface water in Boomerang Lake (Re-measured on April 22, 2003)…… ……34

Table 3d: pH values after storage of cirumneutral surface water in Mud Lake (Re-measured on March 17, 2003)…….……..35

LIST OF FIGURES

Figure 1a: Phase diagrams of groundwater where pH values changed 0.5- 2.0 units (after Dold 2000)……. 24

Figure 1b: Phase diagrams of groundwater where pH values changed more than 2.0 units (after Dold 2000)…….....25

Figure 2a: Mineralogical analysis of precipitates for M7N, Sampled September 1999…. 27

Figure 2b: Mineralogical analysis of precipitates for M7N, Sampled May 2001…… 27

Figure 2c: Mineralogical analysis of precipitates for M7S, Sampled May 2001…… 28

Figure 2d: Mineralogical analysis of precipitates for M27C, Sampled May 2001……..28

Figure 2e: Mineralogical analysis of precipitates for M27S……...29

LIST OF MAPS AND PLATES

Map 1: Overview of South Bay Waste Management Area……..….2

Plate 1: Back fill raise excavated with pipe for underground effluent discharge.… 2

Plate 2: The Backfill raise ditch leading to Boomerang Lake with yellow-boy in Spring 2001…….…….....2

Plate 3: Boomerang Lake Particulate on 0.45µm filter paper (x 10)…….....9

Plate 4: Water bottles with precipitate having formed on the walls during storage …….. .10

Plate 5: Micrograph of slide surface suspended in piezometer M79…….. .21

The acid generation potential of iron precipitates and their sludge in Decommissioning with Ecological Engineering

1.0 Introduction

The Ecological Engineering approach to decommissioning mine sites, which has been applied at the South Bay Waste Management Area (SBWMA), takes advantage of a number of naturally-occurring processes to correct problems associated with acid mine drainage. One of these natural processes is to allow the formation of iron precipitates to occur without adding neutralisation chemicals such as lime as this requires the maintenance of a chemical treatment plant, often in perpetuity. Such plants produce, as a secondary waste, a sludge containing high metal concentrations, which needs disposal.

For South Bay, a former Cu/Zn Mine with tailings and underground workings producing AMD, natural sludge production is estimated to be about 30 m^3 annually. The estimated sludge production for a high-density treatment plant would generate about 1,200m^3 of sludge per year, including spent lime, while a general treatment plant would generate 3000 m^3 per year (Kalin, 2001). The tailings consist of 41 % pyrite and 4 % pyrrhotite and are expected to generate AMD for anywhere between 1000 to 35,000 years. From an economic and environmental viewpoint the Ecological Engineering technology developed at this site in the last 15 years should not be dismissed without careful consideration. Ecological Engineering integrates natural iron - precipitation, alkalinity generation by microbes and biological polishing along with measures to reduce the rates of acid generation.

The objective of this report is to summarize the acidification associated with iron precipitation which occurs in the discharge of contaminated ground water seepages. It will address precipitate formation in mine working discharges to the Backfill Raise Ditch (BRD), in the relevant water bodies of the SBWMA, which include Boomerang and Mud Lakes which have been utilized as polishing ponds and Armanda Lake, inadvertently acidified by effluent from Mud Lake.

1.1 Problem Definition

As the iron precipitates form solid particles, a chemical transformation takes place from iron hydroxide to the stable goethite mineral. This transformation is associated with extensive hydrogen ion formation, which leads to acidification or lowering of the pH (Dold, B 2002). The iron particulates are generally below 1 µm in size and remain suspended in the water column for some time. They adhere easily to any surface, producing a characteristic brown staining. If the transformation to goethite occurs while the precipitates are still in the water column, acidification may result.

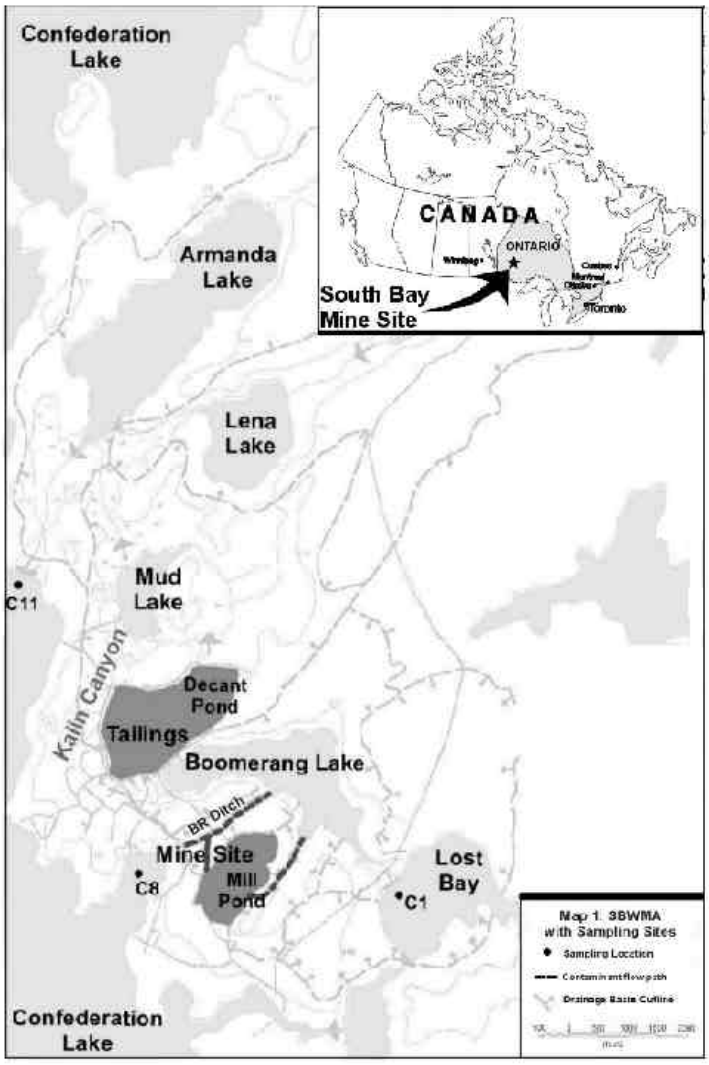
Ground water discharges in the SBWMA occur in three locations. Discharge of the effluent from the underground workings occurs at the Backfill Raise (BRC), as shown in Plate 1. From there it moves to the Backfill Raise Ditch, where iron particulates accumulate as sludge (Plate 2). The acidified water leaves to Boomerang Lake, a biological polishing lake. Boomerang Lake also receives ground water seepage from the tailings.

Plate 1: Back fill raise excavated with pipe for underground effluent discharge

Plate 2: The Backfill raise ditch leading to Boomerang Lake with yellow-boy in Spring 2001

A further ground water plume moves towards Mud Lake, where it discharges by up-welling through a thick layer of organic-rich sediment, approximately 8 m in depth. In Mud Lake the metals accumulate in and on the sediment. Tests are currently underway of an in-situ

microbiological treatment process, which may remove contaminants while still in the ground water plume, prior to its discharge into Mud Lake. Once this treatment is in full operation, Mud Lake will be converted to a biological polishing pond. Armanda Lake received a large pulse of AMD from Mud Lake, as a beaver dam needed to be lowered. The increased water level in Mud Lake was flooding the SBWMA, increasing contaminant generation, as it increased the vadose zone in the tailings. Armanda Lake is expected to recover with minor ecological treatment, once Mud Lake is fully treated by precipitating the metals in the sediment and the reduction of AMD input, due to the in-situ treatment. Map 1 provides an overview of the locations discussed within the SBWMA. The tailings and the water bodies receiving AMD effluent all contain iron precipitates. Their effect on acidification and the stability of the water characteristics is being evaluated.



Map 1: Overview of South Bay Waste Management Area

1.2 Secondary Fe(III) hydroxides, oxyhydroxides, and oxyhydroxide sulfates

The literature on acid mine drainage generally assumes that iron precipitation is a benign process. It reduces the metal concentration in the effluent through either co-precipitation or adsorption of the metals to the particulates forming. The resulting sludge has generally been considered a non-reactive product. This assumption is also made when ABA (Acid Base

Accounting) is carried out for the environmental management of mining wastes. The acid generation potential of the wastes is calculated based on the sulphide content of the tailings or the waste rock. At the onset of this project, some 15 years ago, the same assumption was made, in that iron precipitates were considered stable, hence environmentally benign.

It has become increasingly clear, however, that hydrogen ions are produced not only by the initial precipitation process, but by the transformation of the solid phase, forming ferric hydroxide sulphates (Dold 2002a). The standard ABA estimate does not include the acid potential associated with the iron and sulphate precipitate transformation. Therefore an overview of the potential reactions is required. They are taken verbatim from Dold 2002.

B. Dold, 2002 in "Basic Concepts of Environmental Geochemistry of Sulphide Mine Waste"

"Table 2: Hydrolysis reactions of Fe(III) species and the associated protons produced (from Stumm and Morgan, 1996).

Species	Equation	Fe^{3+}	H^+	log *K* (I = 3 M)
Fe^{3+}		1	0	0
$Fe(OH)^{2+}$	$Fe^{3+} + H_2O <=> Fe(OH)^{2+} + H^+$	1	-1	-3.05
$Fe(OH)_2^+$	$Fe^{3+} + 2H_2O <=> Fe(OH)_2^+ + 2H^+$	1	-2	-6.31
$Fe(OH)_{3\,(aq)}$	$Fe^{3+} + 3H_2O <=> Fe(OH)_{3\,(aq)} + 3H^+$	1	-3	-13.8
$Fe(OH)_4^-$	$Fe^{3+} + 4H_2O <=> Fe(OH)_4^- + 4H^+$	1	-4	-22.7
$Fe_2(OH)_2^{4+}$	$2Fe^{3+} + 2H_2O <=> Fe_2(OH)_2^{4+} + 2H^+$	2	-2	-2.91
$Fe_3(OH)_4^{5+}$	$3Fe^{3+} + 4H_2O <=> Fe_3(OH)_4^{5+} + 4H^+$	3	-4	-5.77

Table 3: Amount of protons produced by the hydrolysis of the different secondary Fe(III) phases.

Phase	Equation	moles H+/mole Fe^{3+} hydrolyzed
amp. $Fe(OH)_3(s)$	$Fe^{3+} + 3H_2O <=> Fe(OH)_3(s) + 3H^+$	3
ferrihydrite	$10\ Fe3+ + 60H2O <=> 5Fe_2O_3.9H_2O + 30H^+$	3
Goethite	$Fe^{3+} + 2H_2O <=> FeO(OH) + 3H^+$	3
Hematite	$2Fe^{3+} + 3H_2O <=> Fe_2O_3 + 6H_+$	3
Schwertmannite	$8Fe^{3+} + SO_4^{2-} + 14H_2O <=> Fe_8O_8(OH)_6SO_4 + 22H^+$	2.75
	$16Fe^{3+} + 3SO_4^{2-} + 26H_2O <=> Fe_{16}O_{16}(OH)_{10}(SO_4)_3 + 42H^+$	2.625
Jarosite	$3Fe^{3+} + K + 2SO_4^{2-} + 6H_2O <=> KFe_3(SO_4)_2(OH)_6 + 6H^+$	2

B. Dold and G. Meinrath, both experts in this geochemical mineralogical field, were consulted for their assessment of the potential acidification that might occur in the SBWMA. They were provided with the same data sets generated for the evaluations presented in this report. Their discussions are given below to ascertain the relevance of the acidification, providing the scientific underpinning to the long-term stability of the proposed natural precipitation suggested as part of the Ecological Engineering remediation approach.

The equations given above describe the processes during precipitation and solids transformation as outlined by Dold. They suggest that on the way to goethite formation, the most stable of the secondary minerals acidification could be severe. Meinrath, on the other hand indicates that "the tailings pore water and the mine site seepages are unique due to elevated concentrations of sulfate. (1.04 – 10.7 g/L of S or about 0.03 – 0.33 mol of SO_4^{2-}, see Table 1). At these levels, sulfate reacts with Fe(III) and competes with hydroxide for binding sites at the ferrous iron ion.

Hence, if sulfate ions bind to ferric iron, newly generated by the oxidation of ferrous iron ions, less hydroxide is generated. For each mol of sulfate bound to Fe(III), one mol H^+ is NOT formed, as often assumed by the formula (1) $Fe^{3+} + 3H_2O <=> Fe(OH)3^o + 3H^+$; in the presence of high sulfate concentrations (2) $Fe^{3+} + 2\ H_2O + SO_4^{2-} <=> Fe(OH)_2SO_4^- + 2H^+$, a reaction which would lead to a lower pH depression.

The hydrolysed aqueous species react further, forming the well-known solids Goethite in case of reaction (1) and the Schwertmannite or Jarosite group solids (e.g. $Fe_8O_8(OH)_6SO_4 \cdot x\ H_2O$) in case of reaction (2). A comparison of the two equations shows that in the case of reaction (1) three formula units of H^+ are formed while in the case of reaction (2) only two formula units of H^+ are formed."

As indicated by the reactions (3), (4), and (5) given below, the conversion of Jarosite to Goethite would generate **3/3 = 1.0** extra formula unit of H+ per formula unit Fe3+; conversion of Schwertmannite(I) to Goethite would generate **6/16 = 0.375** extra formula unit H+ per formula unit Fe3+; and conversion of Schwermannite(II) to Goethite would generate **2/8 = 0.25** extra formula unit H+ per formula unit Fe3+. Thus the formation of Goethite via Jarosite would generate a total of **(2+1) = 3** formula units H+ per formula unit Fe3+; formation of Goethite via S(I) would generate a total of **(2.625+0.375) = 3** formula units H+ per formula unit Fe3+; and formation of Goethite via S(II) would generate a total of **(2.75+0.25) = 3** formula units H+ per formula unit Fe3+. Those total amounts **are the same as** the **3** formula units H+ ions produced per formula unit Fe3+ in the direct formation of Goethite.

Formation of Jarosite requires very high sulfate concentrations. It is unlikely that large quantities of this precipitate will be found in the BRD ditch. Samples from the ditch will be collected for investigation of the solids phases to confirm or refute the conclusion.

Dissolution of sulfate minerals

Iron sulfate minerals

Jarosite => Goethite: $KFe_3(SO_4)_2(OH)_6 \Rightarrow 3FeO(OH) + K^+ + 2SO_4^{2-} + 3H^+$ (3)

Schwertmannite (I) => Goethite: $Fe_{16}O_{16}(OH)_{10}(SO_4)_3 + 6H_2O \Rightarrow 16FeO(OH) + 3SO_4^{2-} + 6H^+$ (4)

Schwertmannite (II) => Goethite: $Fe_8O_8(OH)_6(SO_4) + 2H_2O \Rightarrow 8FeO(OH) + SO_4^{2-} + 2H^+$ (5)

Thus, due to the high sulphate levels, precipitates different from the common iron hydroxides, oxyhydroxides and oxyhydrates (as, e.g., FeOOH (goethite) and Fe_2O_3) will form in the tailings. The extent to which these Fe(III) sulphate minerals form is rather difficult to assess.

Unfortunately, the Fe(III)-H_2O-S(VI)-system is not well investigated with respect to the quantitative thermodynamic data of hydrolysis and sulphate complexation. Technical difficulties in the investigation of the extremely hydrolysable Fe(III) are discussed in Meinrath & May, (2001). Both in the tailings and with the seepages from the mill site (1702.67 mg/L sulphate and 49.64 mg/l Fe discharging from BRC) both high in sulphate, it is likely that goethite is the predominant precipitate."

From the mineralogical considerations it is clear that iron precipitates represent a very complicated mineral group. According to Dold: "Iron precipitates form under conditions ranging from pH 1 to alkaline. Most are not considered stable, although they are believed to be meta-stable and will transform in time. The transformation of Schwertmannite to Goethite can be very fast (hour to days). The controlling parameters of the kinetics are not well understood. Overall, the total amount of protons is the same if goethite is instantly precipitated and/or if Jarosite is precipitated first followed by the transformation to goethite per mole ferric hydrolyzed. The transformation is important, and must be taken into account when assessing the acidification. It becomes clear, that the sequence and the conditions of the transformation is of importance in a system such as SBWMA, where physical transport of the precipitated mineral phase does take place." At the site, the principle pathways are from the tailings to the polishing pond and/or to the sediment.

1.3 Geochemical modelling

As one starts to understand the processes of iron and sulphate precipitate formation, the associated acid generation potential in the tailings pore water and ground water seepages becomes relevant. Geochemical investigations of tailings porewater and contaminated groundwater using PhreeqC were carried out for the tailings. Geochemical modeling of the pore-water suggests that the dissolution of secondary precipitates and minerals is taking place and pH depressions were noted. The results also suggest that in the tailings pore water, a continuous cycling of secondary minerals in the vadose zone of the tailings might take place in spring and fall with the arrival of fresh water. This could mean that the timeframe, which can be expected for acid generation based on ABA, would be extended, since in the case of continuous cycling, the acid generation potential is never depleted. As this would be an important observation, the

reliability of the geochemical model needs to be evaluated further. The acid generation potential and its longevity is of utmost relevance to the remediation measures. Meinrath (2003) reviewed geochemical models in detail.

According to Meinrath "the accepted probabilistic modelling such as PhreeqC does produce interesting results, but the behaviour of the solid phases (or the precipitates) is unpredictable. As was indicated from the previous discussions the area of iron mineralogy is complex. The solubility products of the solid phases are known only with large uncertainties. The number of solids in the Fe(III)-H_2O-O-S(VI)-A (where 'A' represents the Alkali metal ions) is very large. The common prediction codes (e.g. PhreeqC, MINEQ, EQ3/6) are thermodynamic equilibrium codes and do not consider kinetics.

In nature however, the precipitate phases are formed predominantly according to kinetic principles. Hence, a system doesn't transform to the most stable system immediately but prefers to transform into the 'thermodynamically closest' form. The thermodynamically most stable phase is eventually reached by solid phase transformations. This behaviour is well known as the 'Ostwald Rule'. The predictability of such solid phase transformations is, therefore, very limited. PhreeqC is not very dependable in the present case, as PhreeqC is a mean-value based modeling program that uses the modified Davies equation for ionic strength correction. For tailings pore-water with up to 0.3 mol L^{-1} sulfate and comparable iron concentrations, the Davies equations cannot be used. PhreeqC is a good model for ground water with low ionic strengths. It would be more appropriate to state that a PhreeqC modeling has shown that dissolutions may take place if the sulfate concentration in the water is lower, as is the case in Boomerang Lake. In summary from the arguments presented above:

- the mean value calculation;
- the unknown reliability of the formation constants;,
- the fact solid phase transformations are kinetically controlled;
- the inadequate use of the modified Davies equation for ionic strength correction;

all indicate that the geochemical modeling results for the tailings may **not** reflect reality and that, in fact, mineralogy of the iron precipitates has not been defined well enough to justify conclusive statements with respect to their acidification potential. Both Dold and Meinrath

agree, however, that the formation of hydrogen ions in the transformation process of iron and sulphate minerals is well documented. However to connect the scientific understanding to a real system such as the SBWMA and its remediation efforts is a challenge and, given present knowledge, cannot be conclusive.

Furthermore, from the author's perspective, the previously considered geochemical/ mineralogical reactions omit the important role of the bacteria, the mainstay of Ecological Engineering**.** Ecological Engineering is a scientifically based approach to decommissioning acid generating sites and the geo-microbiological role in acid generations is a significant consideration in the treatment processes proposed and tested for the SBWMA. It is nessessary that all aspects of contaminant generation - in this case the generation of hydrogen ions – be considered as well as the natural counterpart to acidification, that is, the geo-microbiological processes which generate alkalinity. Only the incorporation or recognition of all components in the remediation system, can lead to a progressively improved ecosystem in the SBWMA. In Section 3.2, the microbiological investigations in the tailings pore water are presented and discussed.

1.4 Assessing acidification due to iron precipitate formation

It is quite evident that although the knowledge base relating to iron precipitation processes is rapidly expanding, it does not yet assist greatly in addressing the stability of sludge and surface water in the SBWMA. When the sulphate concentrations are not as high as in the tailings, such as in the polishing ponds, the reactions of precipitate formation and the associated acidification may differ.

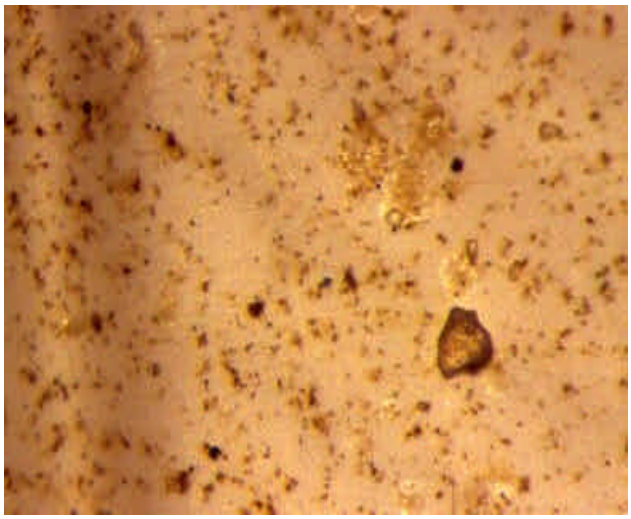


Plate 3: Boomerang Lake Particulate on 0.45µm filter paper (x 10)

Practically small yellow-boy particles accumulate on the 0.45 µm filter paper, both in surface and groundwater and particles form during storage on the walls of bottles (Plate 3 and 4).

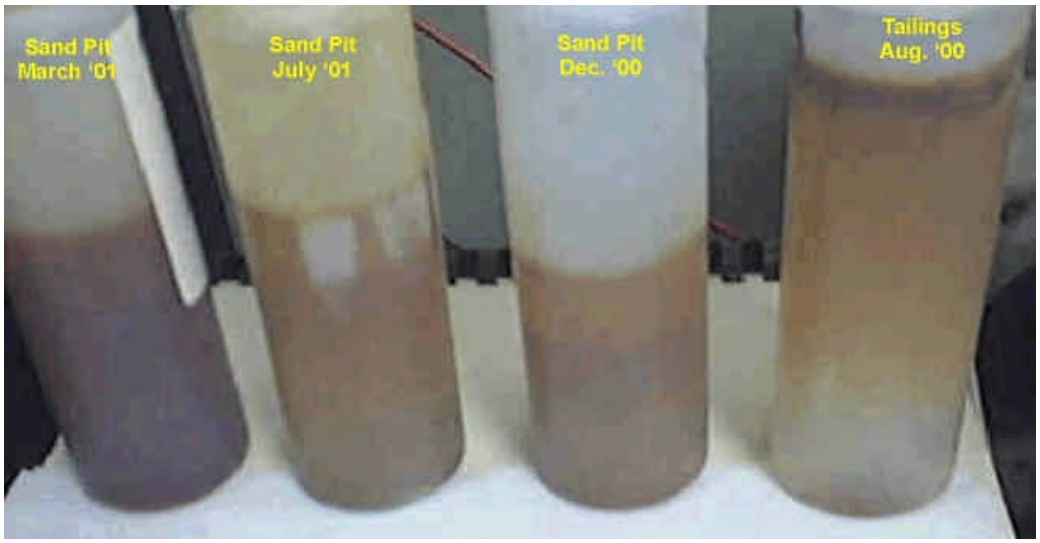


Plate 4: Water bottles with precipitate having formed on the walls during storage

A pragmatic, empirical approach to address the acidification due to the mineral precipitation processes can provide a realistic answer to the question of acidification. It is postulated that if iron and sulphate precipitation causes the severe acidification of ground and surface waters, it should be evident through a comparison of the pH values in freshly collected water and the pH of the same water containing the particles after a certain storage time.

Therefore water samples have been stored in dark conditions, both from the piezometers (tailings pore water with the highest sulphate concentration) and samples from all relevant water bodies in the SBWMA, representing lower concentrations of sulphate. The pH values in the samples are determined at different time intervals. Closed bottle conditions reflect a worse case scenario for the acidification of the water, as in the field natural buffer activity is present, through incoming water and biological activity. If the pH values decrease with time, a potential

for acidification exists. If the pH value stays within the error of the measurement or if it is higher, then acidification is not of concern.

2.0 Materials and Methods

2.1 Sample collection sites.

The samples held in storage were taken from Confederation Lake, Boomerang Lake, Armanda Lake, Mud Lake and Decant Pond. Confederation is the lake to be protected and serves as a control for the observations. Mud Lake is contaminated by groundwater seepage discharge and is the most acidic lake in SBWMA. Armanda Lake is also acidic, contaminated only with hydrogen ions by a pulse of AMD released from Mud Lake. Boomerang Lake is acidic, and serves as a biological polishing pond. Similarly, Decant Pond, located on the tailings, has been functioning as a biological polishing pond. Ground water is collected from piezometric wells located in the tailings. Water running along the Backfill Raise ditch is also considered in this investigation. These sampling locations are all relevant sites for the iron precipitation process and are presented in Map 1.

2.2 Water sample collection and storage

Surface water was collected as 'grab' samples 0.5 m below the surface of the water body. The filtration and acidification with nitric acid was carried out on duplicate samples immediately. The samples were filtered through 0.45 µm and both filtered and unfiltered whole samples were acidified with nitric acid. Unpreserved samples were also shipped to the laboratory, on which the re-measurements were taken on arrival in the Boojum laboratory in Toronto and later after storage.

Groundwater samples were taken before and after bailing with a standard bailer from piezometers installed at various locations in the tailings. Samples were collected between the years 1996 to 2003. Generally when a tailings groundwater campaign was carried out, the bailing was drawn from the piezometers in sequence by hydraulic conductivity, from a slow to fast recharge rate. Bailing of all relevant piezometers in the tailings area takes more then 24 h.

Sampling starts after all piezometers have been bailed. They were then sampled in reverse order from fast to slow in order to obtain a nearly simultaneous snapshot of the entire area. Samples were analyzed in a field laboratory so that the time lapse between retrieval and measurement was generally between five and 30 minutes. All samples were stored in a cooler with ice.

Both groundwater and surface water samples were stored in 250 ml polyethylene bottles with screw caps containing a foam liner at room temperature at 20'C. The bottles are not airtight and ample air space was present above the water in the bottles in all cases. The chemistry of the samples (pH, Em, EC and temperature) was re-measured at various time intervals.

For the tailings pore waters, retrieved from the piezometers, iron oxidation occurs within minutes and iron precipitates are formed, accompanied by a rapid change in redox potential. An initial acidification was noted and pH development was followed carefully. After an initial determination of pH, conductivity, E_H and temperature in the field and again in the laboratory, the samples were stored in darkness at room temperature. While in storage, iron precipitate progressively covered the walls and bottom of the bottles. The tailings pore waters stored in bottles containing precipitates were therefore measured several times over a period of 4 years. The presence of microbes in the stored bottles with the iron precipitates and in the tailings pore water was tested.

2.3 Instrumentation and measurement procedure

The conductivity measurements were performed using an OAKTON Con 400 series EC instrument set to mS or µS mode that also reads temperature. The conductivity probe was calibrated for a conductivity range of 0.001 to 19.99 mS at 25 ^oC, and wiped with isopropyl alcohol and rinsed with deionised water after a minimum of every 100 samples. The probe was tested in standard solutions of 50, 500 and 5,000 µS covering the range of conductivities encountered in the sample set.

A Corning 315 pH/Ion pH meter equipped with a combination electrode also by Coring #33221 -034. T he pH probe was calibrated with buffers at pH 4 and 7 prior to pH determination. A Corning M103 redox instrument with an inert platinum electrode and a standard Calomel probe was used to determine E_H. The pH and E_H probes were stored in saturated KCl solution. Redox

potential readings were recorded as Em in millivolts units and were transformed to E_H where E_H = Em +[241 –0.66*(T ^oC-25 ^oC)] (Em means measured potential).

Fifty ml of each sample was poured into a 120 ml container within which all three probes (pH, Em, EC and temperature) were submerged until readings were stable, usually within 5 seconds. After the measurements were completed, all three probes were rinsed thoroughly with distilled water. The measuring containers were washed with tap water, followed by thorough rinsing with distilled water.

After measurements were taken, the sample was poured back into the original bottle containing the remaining stored water sample. The measuring containers were washed in acid baths (5% H_2SO_4) for 24 hours between re-measurement sessions. After chemistry re-measurement, samples were stored back in either storage room or fridge.

2.4. Elemental analysis

The chemical analysis for the elements was generally carried out on the 0.45 µm filtered and acidified water. For one sampling campaign (1996) a data set was generated, in which all whole samples were acidified (WA), and filtered acidified (FA) after the initial Fe precipitation and acidification had taken place. Naturally acidified supernatant samples were filtered and acidified (FAS) after the pH value was considered as stable. This occurred after 10 days. The FAS samples were also sent for elemental analysis by Saskatchewan Research Council Analytical Services Laboratory in Saskatoon, Saskatchewan, a certified laboratory. Duplicate and or spiked samples are shipped to the laboratory occasionally, where internal QA/Qc procedures are in place.

2.5. Microbiological isolation and enumeration

Water from the stored samples with particulates was shipped to B. Johnson Laboratory at the University of Bangor, Wales U.K. The samples were processed after Johnson (1995) using a media for enumerating acidophilic bacteria. Glass slides from four sites (M7S, M7N, M27C and M27S) were shipped immediately after collection in the field in their original water. For each slide an area of 55 mm by 26 mm was cleared using sterile cotton wool swabs. These were placed into 5 ml of sterile basal salts solution (pH 5.8) and vortexed thoroughly to release the trapped bacteria.

A dilution series (10^{o} - 10^{-4}) was prepared from each suspension, and 100 µl aliquots of each used to inoculate solid media that are selective for extremely and moderately acidophilic iron-oxidizing and heterotrophic bacteria (Johnson, 1995; Hallberg and Johnson, 2001). Plates were incubated for 4-6 weeks at 20°C, before colonies were counted and preliminary identification made of isolates.

2.6. Mineralogical analysis

Stored samples with precipitates collected from the tailings pore water were shipped to the University of Lausanne, Switzerland to the Center for Minerals Analysis to be carried out by B. Dold. All samples were characterized by powder XRD using a 3020 Philips diffractometer with Cu K a (l =1.54056 Å) radiation (40 kV, 30 mA) and a diffracted beam with monochromator. Scans were collected using a 0.05 2 step interval and 20 s counting time per step.

2.7. Tailings pore water

The elemental composition of the groundwater samples is presented in Table 1a. The Fe concentrations range from 698 mg/L to 14,300 mg/L. The sulphate concentrations in the selected tailings pore water range from 3,120 mg/L to 32,100 mg/L. The major cations in the tailings pore water are Ca and Mg along with Mn. The major contaminant in the pore water is Zn.

An anion/cation balance of the water was calculated as a check on the accuracy of the analysis (Table 1 b). The errors range from 0.57 % to 3 % for most samples, with the exception of errors as high as 7 % to 11 % for 4 samples from the dataset.

The first re-measurement of pH was carried out in 1999 on groundwater samples collected in the summer in 1996. In Table 1c, the pH value measured in the field is given in the first column and the re-measurement is presented in the second (1999) and third columns (2000).

3.0 Results and Discussion

The results are presented first for the tailings pore water, considering the geochemical precipitation reactions followed by the results of the microbiological investigations in the tailings

pore water. As microbiological activity is evident, the questions of the potential precipitate identification was addressed by fitting the stored pH and E_H values of the water to phase diagrams for sampling period measurements (0 to 30 minutes) and the measurements obtained in samples stored up to 4 years. A shift in the values suggested that indeed in some pore-water samples conditions were conducive to the formation of precipitates leading to significant acidification due to Schwertmannite formation; accordingly the mineralogy of selected precipitates is identified for some samples from the tailings. Lastly the pH values for the surface water bodies are presented, along with the E_H values and the electrical conductivity, comparing values for freshly collected and subsequently stored samples. The water of the clean water bodies of the SBWMA are presented first for Confederation Lake and Decant Pond (Table 3a), secondly the values for Armanda Lake, contaminated only with hydrogen ions, are presented (Table 3b). This data set is followed by values from water bodies within the SBWMA with increasingly more contaminated and acidic water bodies ending with the comparisons of the values obtained for Mud Lake.

Table 1a: Elemental concentration (mg/L) of water samples collected from South Bay tailings area on September 10, 1996

Piez. #	Al	Ca	Fe	K	Mg	Mn	Na	Zn	S	SO_4
H5	0.168	388	1440	26.1	174	21.1	33.2	10.1	1500	4500
H8	30.9	387	9550	10	375	123	8.88	749	7260	21780
M24W	0.7	393	2420	7.4	79	37.5	2.83	59.6	1840	5520
M27N	0.384	362	7800	44.3	304	99.5	16	189	5410	16230
M27S	1.75	331	7350	48.7	275	91	11.4	270	5030	15090
M4	5.98	353	1400	21.5	110	43.6	9	81.2	1380	4140
M40A	0.74	400	698	9.8	59	16.8	3.44	17.7	1040	3120
M5E	1.7	221	1250	10.7	83.5	36.2	4.89	265	1120	3360
M5W	8.2	421	14300	39.5	408	280	8.6	4070	10700	32100
M7N	4.19	370	4060	17.5	128	85.5	4.58	177	2790	8370
M7S	1.01	419	4950	36.2	373	141	14.4	399	4970	14910
H6	5.75	390	5650	9.3	295	136	7.42	310	4920	14760
H7	3.43	400	1470	6.5	117	37.2	4.4	95.8	1620	4860

Table 1b: Elemental concentration (epm) of water samples collected from South Bay tailings area on September 10, 1996

Piez. #	Al	Ca	Fe	K	Mg	Mn	Na	Zn	S	Cations	Error
H5	0.02	19	52	0.67	14.32	0.77	1.44	0.31	94	88.5	-2.81%
H8	3.44	19	342	0.26	30.86	4.48	0.39	22.9	453	423.6	-3.34%
M24W	0.08	20	87	0.19	6.50	1.37	0.12	1.82	115	116.4	0.68%
M27N	0.04	18	279	1.13	25.02	3.62	0.70	5.78	337	333.7	-0.57%
M27S	0.19	17	263	1.25	22.63	3.31	0.50	8.26	314	315.9	0.33%
M4	0.67	18	50	0.55	9.05	1.59	0.39	2.48	86	82.5	-2.14%
M40A	0.08	20	25	0.25	4.86	0.61	0.15	0.54	65	51.4	-11.55%
M5E	0.19	11	45	0.27	6.87	1.32	0.21	8.11	70	72.8	2.03%
M5W	0.91	21	512	1.01	33.57	10.2	0.37	125	667	703.7	2.64%
M7N	0.47	18	145	0.45	10.53	3.11	0.20	5.41	174	184.0	2.79%
M7S	0.11	21	177	0.93	30.69	5.13	0.63	12.2	310	247.9	-11.14%
H6	0.64	19	202	0.24	24.28	4.95	0.32	9.48	307	261.7	-7.95%
H7	0.38	20	53	0.17	9.63	1.35	0.19	2.93	101	87.3	-7.33%

Table 1c: Potential pH development in groundwater from tailings on Sept. 10, 1996

Piez. #	pH History			Potential pH Development				
				IF all original [Fe] was Fe^{2+} then pH could drop to pH units due to				pH after PHREEQC equilibrium with CO_2 O_2 and goethite
	pH field '96	pH '99 from '96	pH '00 from '96	oxid.& precipitates of Jarosite	oxid.& hydrol. to $Fe(OH)_3$	precipitation of Jarosite	hydrolysis to $Fe(OH)_3$	units
H5	4.63	2.34	1.91	1.59	1.29	1.29	1.11	1.59
H8	4.82	2.18	1.84	0.77	0.47	0.47	0.29	1.12
M24W	5.09	2.03	1.82	1.36	1.06	1.06	0.89	1.39
M27N	3.57	2.17	1.76	0.85	0.55	0.55	0.38	1.15
M27S	5.09	2.24	1.85	0.88	0.58	0.58	0.40	1.16
M4	3.84	2.10	1.93	1.60	1.30	1.30	1.12	1.55
M40A	3.02	2.15	1.96	1.87	1.59	1.59	1.42	1.18
M5E	5.60	2.27	1.93	1.65	1.35	1.35	1.17	1.61
M5W	4.97	1.99	1.63	0.59	0.29	0.29	0.11	1.06
M7N	4.19	2.29	1.85	1.14	0.84	0.84	0.66	1.26
M7S	3.65	2.24	1.84	1.05	0.75	0.75	0.57	1.28
H6	5.36	2.20	1.79	0.99	0.69	0.69	0.52	1.23
H7	5.52	2.20	1.86	1.58	1.28	1.28	1.10	1.60

Clearly oxidation had taken place along with a significant drop in pH. In the remainder of Table 1c, the expected pH values from the stoichiometric calculations are presented using the iron concentration in the water samples. The pH values when recovered in the field range between 5.6 to 3.0, where the lower values represent highly-reductive, deep, tailings pore water. After 4 years of storage most pH values have decreased to a pH value of 1.8 units. The expected pH values could, however, be as low as a pH 0.38, a value not attained in any of the samples. Generally, none of the samples reached the expected low pH value, if it is assumed that all the iron in the tailings pore water is present in its reduced form, Fe^{2+}.

Four (4) types of precipitation reactions were considered as outlined previously but excluding the formation of Schwertmannite. The transformations to this mineral had not been documented anywhere at that time or, at least, had not reached mining waste management literature.
From the estimates of potential pH values it could be expected that even after three years in storage the expected low pH had not been reached. Although a further drop in pH was noted with the third measurement in 2000, it was still not as low as might have been expected based on the stoichiometric assessment.

According to Meinrath and Spitzer (2000) the uncertainties associated with the two-point pH calibration procedure and the high ionic strength of the piezometer pore water samples, produce a high bias in the pH values where $pH = - \log a_{H^+} = - \log c_{H^+} + \log \gamma_{H^+}$. The activity coefficient in high ionic strength waters is different from the activity coefficients in the buffers used for calibration of the pH probe. Therefore low ionic strength calibration buffer solutions can lead to large differences in pH measurements. Further, the authors suggest that a bias is introduced by high liquid junction potentials. As a consequence the pH values carry considerable uncertainty. Thus the noted differences between the expected and measured pH values might not be as large as they appear or could be an artefact of the measurements.

This consideration is not exactly helpful to the assessment of acidification, but it may serve as a cautionary note on the pH values observed, at least for highly-saturated tailings pore water. From a practical perspective, regardless of uncertainties in the measurements, the question of

acidification is still relevant to remediation work if pH depressions occur in surface and ground water.

It was concluded (with or without uncertainty in the measurement) that the oxidation/precipitation reactions had not gone to completion and that the causes should be addressed. Although lower pH values might be expected, it is postulated that microbes counteract the acidification by iron reduction. Discrepancies between the expected geochemical result and the reality can often be explained by microbial activity, a possibility completely ignored by previous geochemical considerations.

3.1 Microbes in tailings pore water stored and fresh

To explain the discrepancy between the low pH values predicted by geochemical models and the higher pH values actually measured in the bottles containing precipitates, a microbiological investigation was launched. The results are reported in Section 3.2.1. As a next step, to relate the storage precipitate to the tailings in the SBWMA, slides were suspended in piezometers in the tailings pore-water to the depth at which the precipitates would form and be colonized by bacteria. These results are reported in section 3.2.2.

3.1.1. Microbes in bottles stored with precipitate

When the problem of the stored water bottles with higher than expected pH values was presented to seasoned microbiologists, they were doubtful that life would be found in these highly contaminated tailings pore waters. The scepticism increased when they were informed that the bottles had been stored for 4 years. Nothing, they predicted could survive such conditions. The author however was convinced that if relevant microbial groups were present and viable, they could be isolated and grown from the precipitates in the bottles.

Accordingly, samples were submitted for microbial isolation and identification to B. Johnson at the University of Bangor, Wales, U.K., a specialist in iron bacteria. Table 2a presents the results

of culturing precipitate in selected stored bottles from piezometers. Microbial groups are identified by their presence or absence. The samples were analysed according to standard culturing conditions. Both iron and sulphur oxidizers and iron reducers were present, along with a few fungi and yeasts. After bacteria were found and identified, their populations were enumerated.

Table 2a: Microbial diversity in 4.6-year stored groundwater from tailings *

Piez.#	Iron-oxidizing bacteria			Iron-reducing bacteria		Moderate Fe-oxidizers	Fungi	Yeasts
	Sulfur-oxidizing bacteria	L.ferrooxidans	Heterotrophic bacteria	Sulfur-oxidizing bacteria	Heterotrophic bacteria			
	At. ferrooxidans		Ferrimicrobium	At. thiooxidans	Acidiphilium			
H5	-	-	+	-	+	-	+	-
H6	+	-	-	-	-	-	-	-
H8	+	-	-	+	+	-	-	-
M4	+	-	+	+	-	-	-	-
M5E	-	-	+	-	+	-	-	-
M5W	+	-	+	-	+	+	-	-
M7N	+	-	+	-	-	-	-	+
M7S	+	-	+	-	+	+	-	-
M24W	+	-	-	-	-	-	-	-
M27N	+	-	-	-	-	-	-	-
M27S	+	-	-	-	-	-	-	-
M40A	-	-	-	-	-	-	+	-

* The samples were collected in September 1996 and sent for microbial analysis in May 2001.

The enumerations of the three major, identified, bacterial groups are given in Table 2b. The main iron-oxidizing group was *Acidithiobacillus ferrooxidans*. With these findings, the point was made in principal, that microbes are present and alive and therefore could affect the geochemical processes, by cycling iron from the precipitate to the water. So clearly microbes can survive in

such conditions and affect geochemical processes, by cycling iron from the precipitate to the water.

Table 2b: Enumeration of acidophilic and Fe-oxidizing bacteria in 4.6-year groundwater*

Piez.#	Fe-oxidizing Acidophiles/ml**	Heterotrophic Acidophiles/ml	Moderagely Acidophilic Fe-oxidizers/ml
H5	7.4×10^4	2.0×10^3	5.5×10^4
H6	1.1×10^2	30	1.5×10^4
H8	1.7×10^5	$<10^4$	3.0×10^5
M4	4.0×10^6	$<10^4$	$<10^4$
M5E	1.2×10^7	1.0×10^5	$<10^4$
M5W	4.8×10^4	2.0×10^3	3.0×10^4
M7N	1.0×10^6	1.0×10^5	3.0×10^5
M7S	2.2×10^6	$<10^4$	$<10^4$
M24W	1.2×10^4	$<10^3$	$<10^3$
M27N	1.9×10^5	1.0×10^4	1.6×10^5
M27S	2.4×10^5	1.0×10^3	2.0×10^5
M40A	1.6×10^5	$2.0 \times 10_4$	1.4 x 105

* The samples were collected in September 1996 and sent for microbial analysis in May 2001.

** These isolates were identified as being predominantly Acidithiobacillus ferrooxidans.

The differences in the microbial populations are intriguing, and beg further data collection. For the present objective, their presence and viability is all that is required. The findings suggest that indeed bacteria may utilize precipitates to exist and grow, albeit in low numbers. The presence of heterotrophic bacteria, which are likely functioning as iron-reducing bacteria, is encouraging, from a remediation point of view. If their growth can be encouraged by the provision of an

energy supply, such as organic matter, they may counteract the pH depression. For example, plant growth in and on the banks of the Backfill Raise Ditch would likely help to stabilize the hydrogen ion production.

3.1.2 Microbes in tailings piezometers

The presence of microbes in stored water bottles does not indicate that microbes are also present in the tailings pore-water. It could be only a storage phenomenon. On the other hand it is probable that microbes in the tailings, under less severe conditions are far more active and could be playing a strong role with the precipitates which are postulated to form in the tailings.

In theory, it should not be difficult to identify bacteria in tailings pore water; however free swimming, mobile bacteria are not necessarily those that grow on the surface of secondary minerals or on tailings particles. Since iron precipitates conveniently attach themselves to any available surface area, it was possible to cultivate representative populations by suspending sterile glass slides in the piezometers in the tailings as retrievable colonizing surfaces. The slide depicted in the micrograph in Plate 5, was suspended from September l996 to September 1997, and is densely covered in microbes.

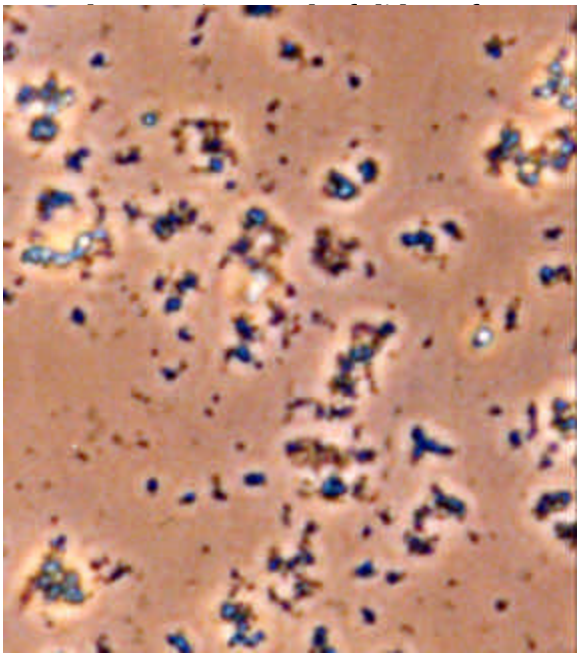


Plate 5: Micrograph of slide surface M79

It was concluded that the methodology would produce representative microbial populations present in the tailings pore water. The same source of bacteria was also used for the in-situ treatment research program conducted with Dr. Ferris at the University of Toronto (Boojum Research Ltd., 2000).

Slides were extracted from selected piezometers with water after they had been suspended for just over four years, from the 10th of June l998 to the 6th of July 2002, at the screen depth of the piezometer. Table 2c presents the enumerations conducted by B. Johnson using the methodology described previously for the stored samples.

Table 2c: Densities of microbial groups on slides installed in piezometers

Piez. #	Stratigraphy	Depth (m)	Date			Fe-oxidizing acidophiles	Heterotrophic acidophiles	Moderately acidophilic Fe-oxidizers
			Slides installed	Slides collected	Slide microbial determined	x 10^3/cm^2	x 10^3/cm^2	x 10^3/cm^2
M7N	Tailings	4.4	Jun-98	Jul-02	Aug-02	59.2	15.7	69.6
M7S	Sand	10.3				139	1.4	<0.1
M27C	Gravel	11.3				0.35	0.7	0.7
M27S	Peat	4.5				8.7	1	3.5

(i) All of the extremely acidophilic isolates from M7S were *Acidithiobacillus ferrooxidans*-like, and no moderate acidophiles were isolated from the slide from this site.

(ii) *At. ferrooxidans*-like isolates also dominated site M7N, though about 12% of the colonies obtained were *Leptospirillum ferrooxidans*-like.

(iii) Site M27C was dominated by *At. ferrooxidans*-like iron-oxidisers. The dominant heterotrophic isolate was a *Frateuria*-like bacterium, previously found in AMD in Norway (Johnson *et al*., 2001).

(iv) There are two colony forms of iron-oxidisers from site M27S, although both appeared to be *At. ferrooxidans*-like bacteria. The dominant heterotrophs were identified as *Acidiphilium*-like.

The same iron-oxidizing bacterial groups were present on the slides as in the stored samples. The isolates from the slides revealed a considerable variance in the density of the populations. The greatest populations were found in the sandy layer below the tailings in M7S at a depth of 10.3 m. Much smaller populations were found in M27C and M27S. The slide suspended in

Piezometer M27S, was at a depth of 4.5 m; that is, the border between peat and tailings, whereas M27C was screened in gravel at 11.3 m depth. The lowest densities were noted in the gravel aquifer, whereas the highest bacterial populations (139 $x10^3/cm^2$ of Fe-oxidizing acidophiles) were found in a sandy aquifer in M7S.

While the population variations are intriguing, confirmation that the bacteria are, in fact, present is all that is required for the purposes of this study. Bacteria are assuredly playing a role in the acidification and/ or neutralisation of the groundwater in the tailings.

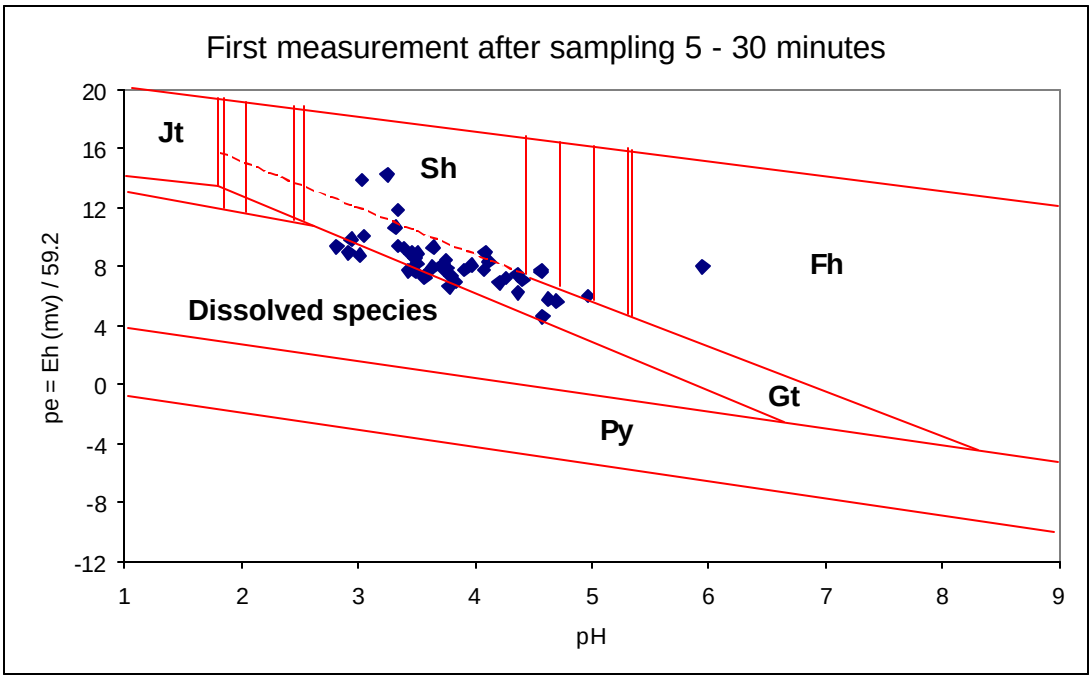
3.2 Mineralogical identifications of iron precipitates

The initial stoichiometric estimates of acidification using Fe^{2+} concentrations and the PhreeqC simulations did not take into account the microbes and the reaction which could be associated with the precipitate Schwertmannite as described by Dold (2002) and referenced above. As this mineral formation can lead to a significant generation of hydrogen ions and hence to a pH depression, it was important to identify if it was indeed present in the storage bottles of tailings pore water. Furthermore, given the scientific debate on the conditions under which this mineral might precipitate, it was considered prudent to identify the mineralogical composition of the precipitates in the stored bottles.

E_H – pH diagrams are generally used to predict the likelihood that a mineral precipitation will take place. Such diagrams give a general idea, but do not consider the required degree of saturation of the solution and the presence of other needed elements to form the precipitate. The data generated from the re-measurement of the stored groundwater samples were fitted to a phase diagram after Dold utilizing pe converted from E_H {pe= E_H (mv)/59.2} and the pH of the water in which the precipitate had formed.

Two groups of samples were considered. The first group consisted of samples in which the pH value changed by 0.5 to 2 pH units for the entire observation interval (Figure 1a). The second group consisted of samples in which the pH value changed by more than 2 units (Figure 1b). The pH/ E_H measurements are presented for an initial period of sampling, at intervals ranging from 5 to 30 minutes, and a second period, covering 0.5 to 4 years in storage, for each of the groups.

Fig. 1a: Phase diagrams of groundwater where pH values changed 0.5- 2.0 units (after Dold 2000)



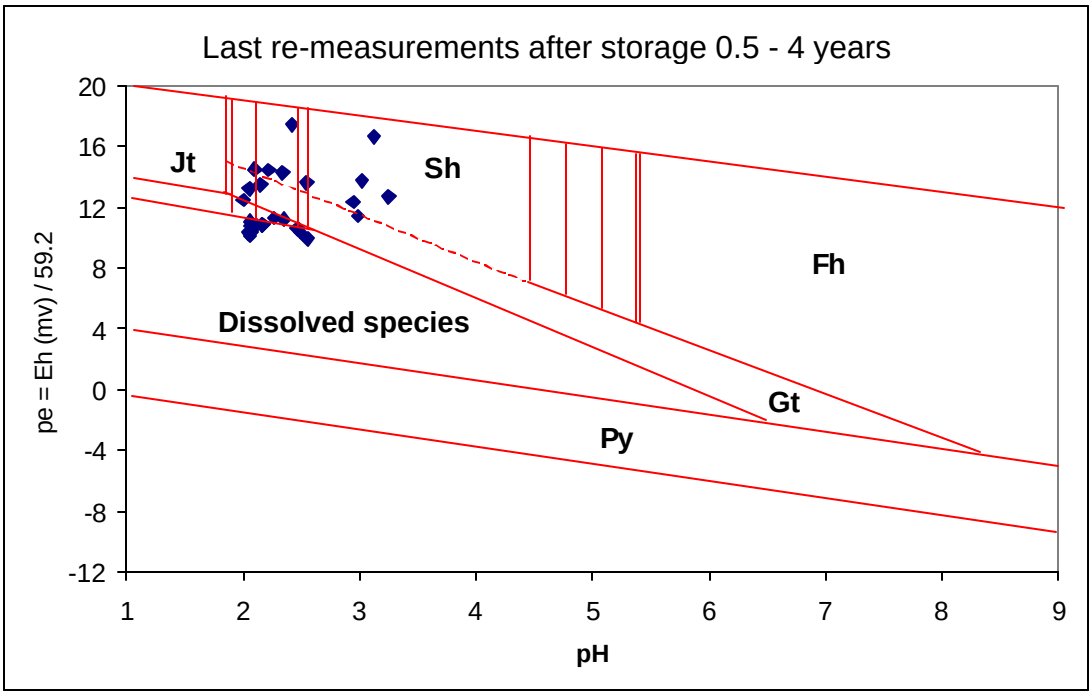
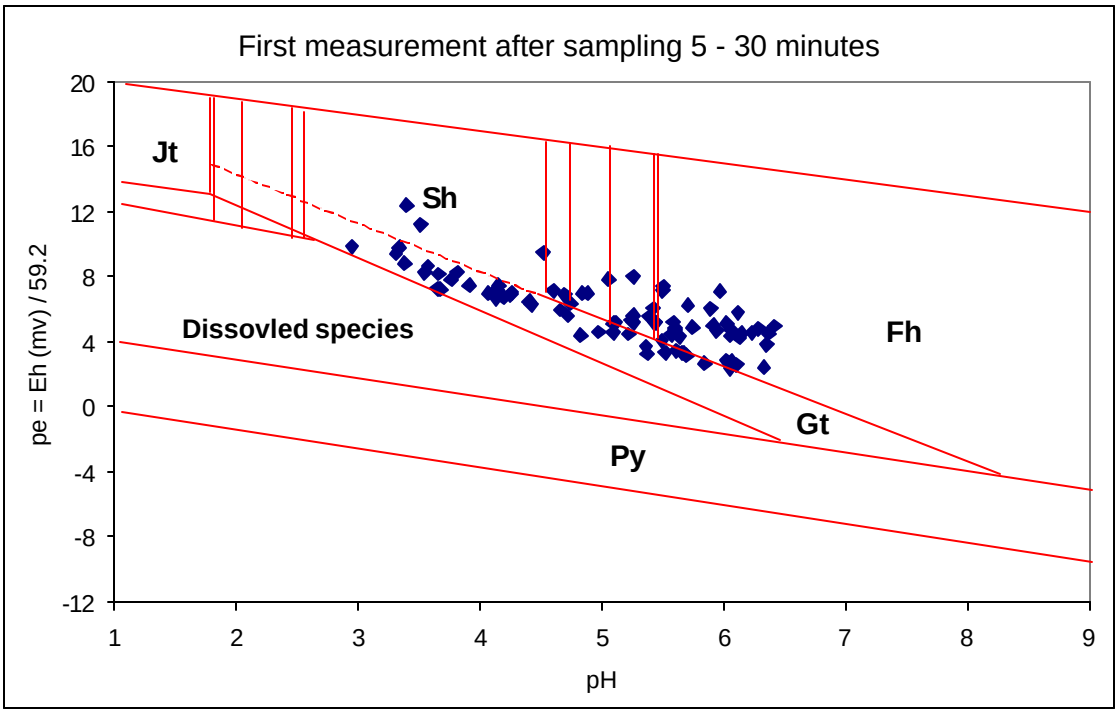
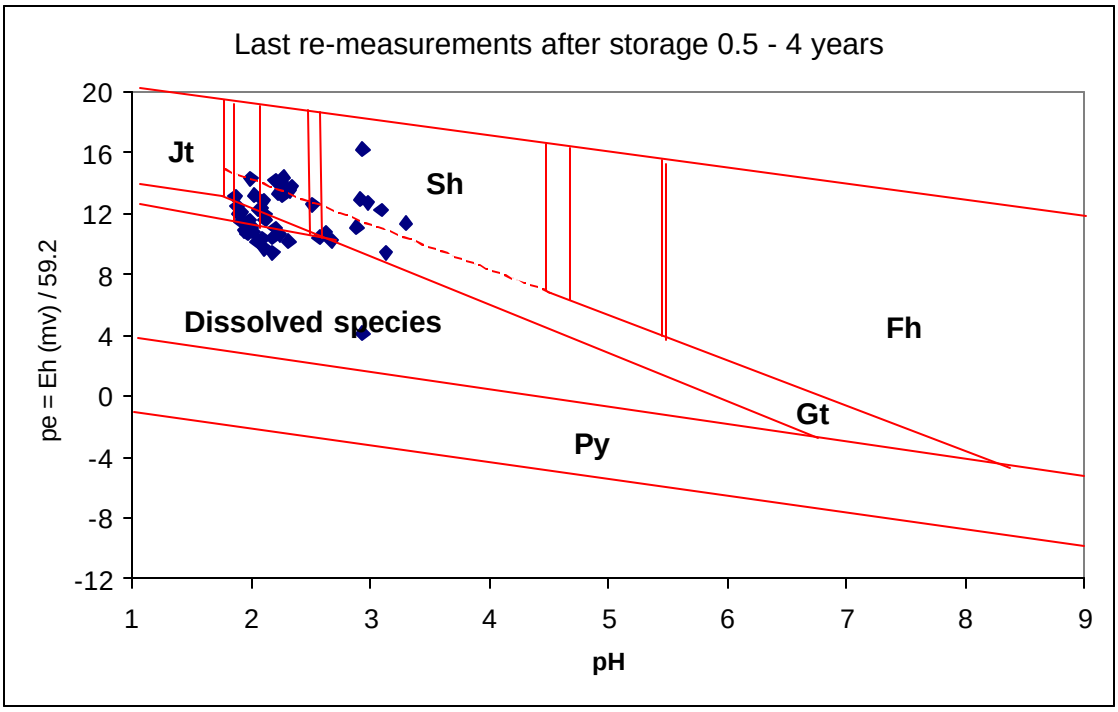


Fig. 1b: Phase diagrams of groundwater where pH values changed more than 2.0 units (after Dold 2000)





The pH /pe of a few samples initially fall in a range in which Schwertmannite might form, but most likely form Goethite. With time in storage, the values shifted into a range conducive to the formation of Schwertmannite and Jarosite. It should be noted, that for the initial period, more data are available than for the samples longer in storage, as more samples were originally measured after sampling, and only a selected set of samples were re-measured over an extended period of time (Figure 1a and Figure 1b).

The main difference between the two sample groups, smaller and larger pH changes, is that those with the larger change, have more precipitates in the iron hydroxide region of the diagram (Figure 1b) than the smaller pH change group. However in both groups, the predominant precipitate is expected to be Goethite and Jarosite, and only occasionally the formation of Schwertmannite is suggested. These observations are somewhat reassuring in that they suggest acidification is unlikely to be of major consequence to the remediation works in progress.

Meinrath expressed caution in the interpretation of the pH/pe diagrams. "It might be unwise to compare data with a large unknown uncertainty, which represent the data set generated here, with almost arbitrary thermodynamic data from unclear sources and unassisted quality, and most likely based on complex computer calculations. Although the data appear to fit nicely, the interpretation may reach the threshold between science and alchemy. This statement is based on the consideration that the uncertainty in lg Ksp($Fe_8O_8(OH)_6SO_4$) is X.Y ± 0.66 from the measurement of pH alone. The 'resolution' of our thermodynamic 'tools' may not allow the presented argumentation." (Personal communication).

Concurrent with the identification of microbial population by Johnson, samples from the same piezometers underwent mineralogical analysis by B. Dold at the University of Lausanne, Switzerland, to identify the composition of the precipitates. Those samples were stored in bottles from May 7th, 2001 to February 4th, 2003 with the exception of M7N-1 which was stored from 2nd of September 1999. In Figures 2a to 2e the results are presented. Although Schwertmannite is present in the precipitate, it is not the major secondary precipitate that is forming.

Figure 2a: Mineralogical analysis of precipitates for M7N, Sampled September 1999

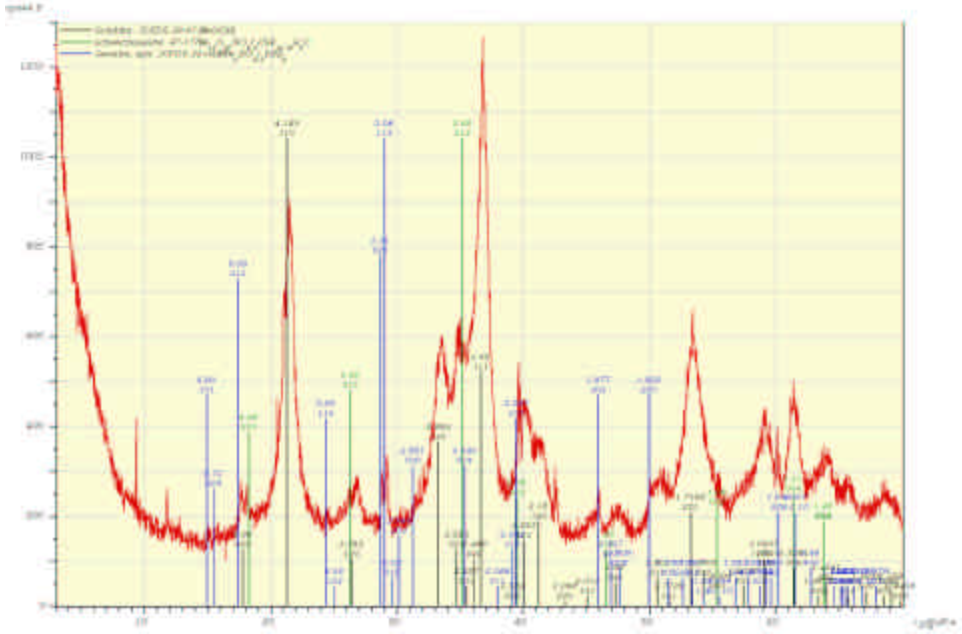


Fig. 2b: Figure 2b: Mineralogical analysis of precipitates for M7N, Sampled May 2001

Fig. 2c: Mineralogical analysis of precipitates for M7S, Sampled May 2001

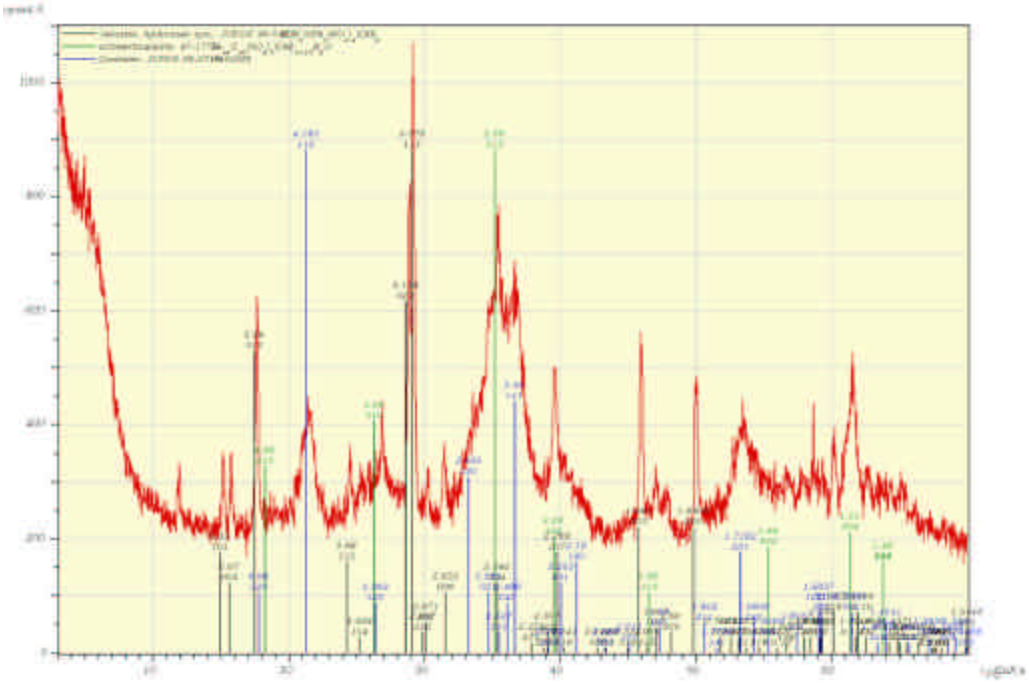


Fig. 2d: Mineralogical analysis of precipitates for M27C, Sampled May 2001

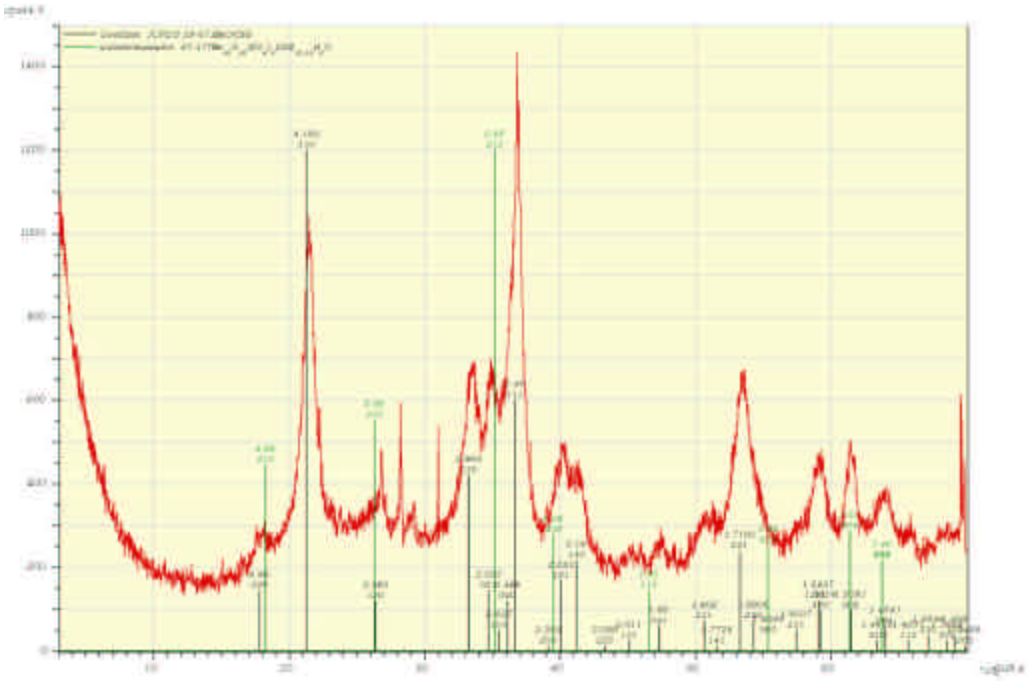
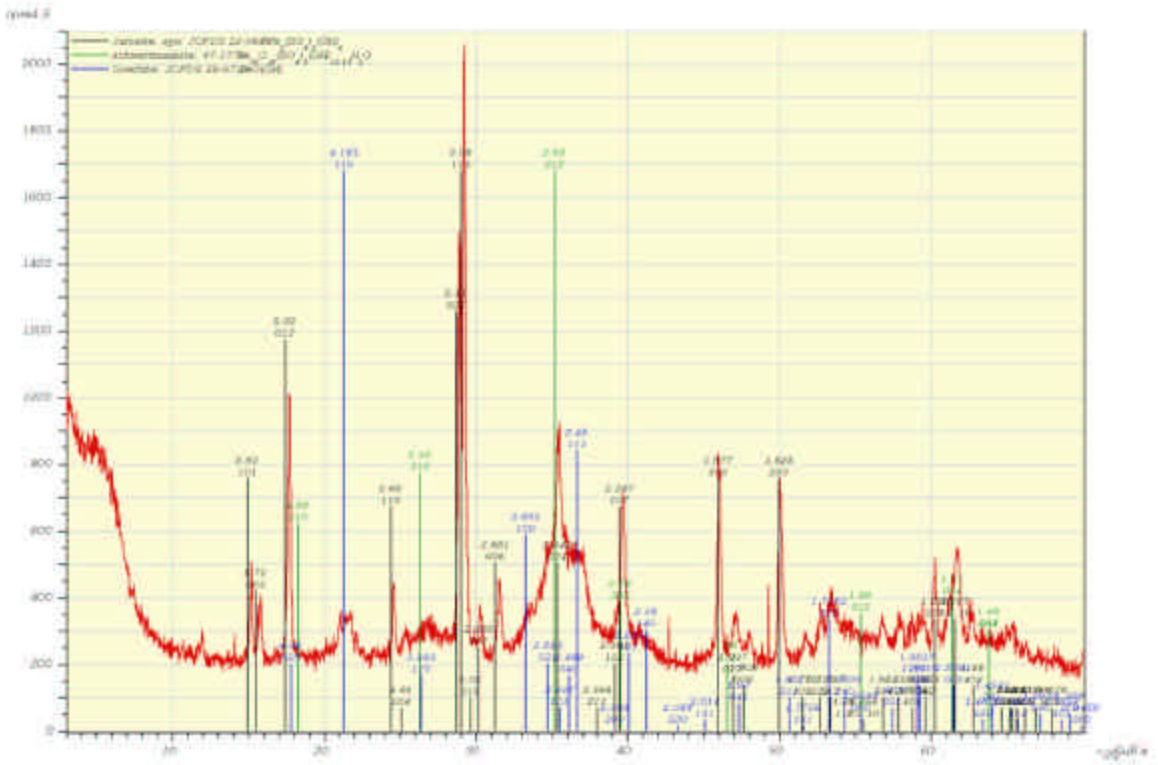


Fig. 2e: Mineralogical analysis of precipitates for M27S



Together with the presence of microbes in the stored bottles, and the mixture of precipitates (Jarosite and Goethite) found along with Schwertmannite the identification of the mineral phases suggest that acidification in the long-term is not a predominant factor which could undermine Ecological Engineering measures suggested for the SBWMA.

3.3. Acidification of surface water samples

With the background on the microbiology and the mineralogy of the iron precipitation, the question of acidification due to the iron hydroxide particulates in the surface water remains to be investigated. This question is also addressed through the measurement of pH in stored samples. It would be expected that if the process of acidification were significant, a depressed pH value would be noted. It is assumed that the particulate to water ratio in the stored water samples is the same as would be the case in the water bodies in the SBWMA. As with the previous samples, the conditions in storage are worst-case scenario. Although this is a pragmatic assumption, iron precipitate distribution is of relevance for Boomerang and Mud Lake. During spring run-off, iron

precipitate sludge from the Backfill Raise Ditch can easily be carried into Boomerang Lake while spring turnover in the lake can suspend iron-hydroxide from the sediments. Particles suspended from the sediment during the spring and fall in Mud Lake, which is very shallow, are carried towards Armanda Lake.

Tables 3a to Table 3d summarize the values for pH, E_H and electrical conductivity. These additional parameters help to substantiate any pH change, which is generally reflected in a change in E_H along with a difference in the electrical conductivity value. The three parameters are presented before and after storage in all types of surface water at SBWMA. Average values of Fe and sulphate concentrations for the surface waters are given along with the name of the specific sampling location in the Tables. The time intervals for which the samples have been stored are not uniform and range from 2 to 4 years.

The concentrations of iron and sulphate in surface water are considerably lower than in tailings pore water. Therefore the quantities of iron precipitates are lower and the effect of a pH decrease should be lower. On the other hand, the geochemical considerations presented in the previous sections suggest that under those circumstances of low sulphate values, the likelihood of Schwertmannite formation, rather than the stable Goethite or Jarosite is higher.

Table 3a presents the original and re-measured pH, E_H and electrical conductivity values for the neutral, clean water of Confederation Lake collected at the monitoring stations C8 in the bay with the mill/mine site beach and at C11. For the circum-neutral, clean water, the pH values increase during storage up to one pH unit, likely due to microbial action and carbon dioxide equilibrium changes. Although some increase is noted in the E_H, the electrical conductivity values remain within the error range of these low conductivity readings.

Table 3a: pH values after storage of cirumneutral surface water in Confederation Lake and in Decant Pond on the tailings (Re-measured on April 22, 2003)

Location	Sampled Date	pH		Eh (mv)		Conductivity (uS/cm)	
		original	re-measured	original	re-measured	original	re-measured
Confederation Lake (Fe=0.24 mg/L; SO_4=26.3 mg/L)							
C8	14-Mar-99	6.17	6.67	571	455	70	67
	25-May-99	7.45	7.39	318	563	57	39.7
	10-Mar-00	6.35	7.55	319	536	60	43.5
C11	8-Dec-98	6.85	6.87	541	531	65	64
	14-Mar-99	6.27	6.82	644	448	89	78.7
	25-May-99	6.83	7.22	657	543	59	41.8
C11 (100')	10-Mar-00	6.15	7.05	422	537	80	64
Decant Pond (Fe=0.70 mg/L; SO_4=375.3 mg/L)							
Outflow	21-Jul-99	6.41	7.81	489	562	363	326
	4-Oct-99	6.90	7.10	478	448	450	498
Beach	21-Jul-99	6.50	7.76	494	577	419	363
	27-Jun-99	7.30	7.15	758	248	428	490
	21-May-01	5.91	6.92	457	610	513	429

Re-measured in April 2002.

A second neutral and relatively clean water body is that of Decant Pond on the tailings, where an ARUM (Acid Reduction Using Microbiology) beach was installed to counteract the tailings seepages entering the pond. Wood waste was placed in the area of the seepage in 1992, which prevented the acidification of Decant Pond which acts as a biological polishing pond. Iron precipitates, of course, have extensively stained the ARUM beach, so the water could be prone to acidification. Re-measurements indicate that after 3.5 years of storage the pH values have not changed, the E_H values have remained the same or increased slightly, but that electrical conductivity remained the same, suggesting that there are no major chemical changes taking place in the water during storage (Table 3a).

In Table 3 all pH values, taken as soon as possible after collection and after time in storage are given along with the E_H and electrical conductivity values for Armanda Lake. This lake is considered endangered by acidification, since its shores are covered with iron precipitates. In 1998, Armanda Lake received a large pulse of AMD from Mud Lake with relatively high iron

concentrations (98 mg/L) when a beaver dam blocking the outflow from Mud Lake had to be lowered.

Table 3b: pH values after storage of cirumneutral surface water in Armanda Lake (Fe=1.99 mg/L; SO4= 118.37 mg/L) (Re-measured on April 22, 2003)

Location	Sampled Date	pH		Eh (mv)		Conductivity (uS/cm)	
		original	re-measured	original	re-measured	original	re-measured
Inflow (#1)	21-May-01	5.59	7.01	576	507	38	26.3
	16-Sep-01	5.99	7.07	443	501	43	**97.2**
ML 52 (#2)	1-Feb-01	4.04	3.78	625	772	332	268
	21-May-01	3.85	3.83	669	659	285	161.5
	16-Sep-01	3.48	3.55	707	646	276	290
ML 43 (#3)	31-Dec-00	3.99	3.80	636	689	263	272
	1-Feb-01	4.09	3.78	635	731	369	191.2
	21-May-01	3.83	3.61	659	639	330	346
ML 11 (#4)	1-Feb-01	5.06	5.00	544	645	238	134.5
	21-May-01	3.88	3.59	663	687	308	312
	16-Sep-01	3.53	3.46	736	537	306	309
ML 51 (#5)	1-Feb-01	4.45	4.11	608	688	327	185.8
	21-May-01	4.05	3.55	649	720	287	310
	16-Sep-01	3.59	3.52	729	684	298	310
ML 44 (#6)	1-Feb-01	4.07	3.78	613	740	346	283
	21-May-01	6.12	5.66	554	570	37	51.6
	16-Sep-01	3.56	3.43	729	694	307	321
ML 30 (#7)	1-Feb-01	4.23	4.03	593	706	326	172.6
	21-May-01	3.74	3.78	678	677	320	297
	16-Sep-01	3.53	3.41	743	713	330	340
ML 10 (#8)	1-Feb-01	4.36	4.09	635	595	293	145.7
	21-May-01	3.32	3.79	735	769	614	795
	16-Sep-01	3.60	3.44	737	714	315	316
ML 53 (#9)	21-May-01	3.21	2.68	732	783	966	1116
	16-Sep-01	3.59	3.40	744	722	320	355
ML 54 (#10)	21-May-01	3.64	3.35	701	786	417	413
	16-Sep-01	3.62	3.40	730	732	320	355
Mixture (ML11,43,44,51,52)	1-Feb-01	4.01	3.98	633	758	331	183.4

Re-measured in June 2003.

The clean inflow water to Armanda Lake is circum-neutral with pH 5.5. Visually the water is brown from the humic substances in a large muskeg area in the upper reaches of its drainage basin. Humic substances can provide some buffer capacity to hydrogen ions, as can be noted by a pH increase of nearly 1.5 units during storage. The water samples from Armanda Lake acidified slightly during the storage, decreasing in pH units about 0.1 to 0.3 during storage. Albeit the small decrease, it is suggesting that the discharged particulates from Mud Lake do contribute to acidification. The inconsistent readings of electrical conductivity for the dates of water sample collected February and May 2001 are due to an error. The second reading in 2003 was obtained with the new Oakton conductivity meter, whereas in 2001 the values originated from the old YSI meter. For this instrument, these low electrical conductivity values are prone to errors within a 100 uS/cm (Table 3b). From the September 2001 collection of samples, stored until June 2003 the pH depressions are minor and for this data set, the E_H and the electrical conductivity is consistent with the pH changes.

For Boomerang Lake (Table 3c), which has higher iron and sulphate concentrations, the pH values and their re-measurement are presented for four sampling locations. The pH changes with storage are in the same order as Armanda Lake (0.1 to 0.2 units) although the sulphate concentration is much higher (424 mg/L compared to 118 mg/L). Here E_H and electrical conductivity reflect changes as they occur. It is suggested that both Armanda and Boomerang Lake are not prone to acidification; many samples in both data sets remain at the same pH value. It should be noted, that the previously discussed buffer bias of the electrode does not apply to these very dilute samples, which makes the measured pH values more reliable than for the tailings samples.

Three samples from the endpoint of the Backfill Raise Ditch (BR 2.5) are presented at the bottom of Table 3c. As the Backfill Raise Ditch has the most variable conditions with respect to the accumulation of sludge (spring and fall rains and summer droughts) the pH changes are presented for the three discreet samples. For this water, the sulphate concentrations are quite high, representing the lower range of sulphate concentrations found in the tailings. However the

pH depressions during storage are not greater than in Boomerang Lake, ranging from 0.2 to 0.4 units (Table 3c).

Table 3c: pH values after storage of cirumneutral surface water in Boomerang Lake (Re-measured on April 22, 2003)

Location	Sampled Date	pH		Eh (mv)		Cond (us/cm)	
		original	re-measured	original	re-measured	original	re-measured
Boomerang Lake (Fe=7.54 mg/L; SO_4=424.4 mg/L)							
B11	23-May-99	3.27	3.11	762	807	939	835
	24-May-99	3.29	3.10	779	726	884	795
	10-Mar-00	3.26	3.11	564	735	900	825
B1	9-Oct-00	3.23	3.14	661	764	700	557
B4	23-May-99	3.27	3.09	780	812	899	781
B10	26-Mar-98	3.31	3.38	730	685	923	894
	8-Dec-98	3.24	3.11	726	848	939	993
	23-May-99	3.28	3.03	767	651	901	749
	11-Mar-00	2.81	3.05	661	693	960	855
Backfill Raise Ditch (Fe=49.64 mg/L; SO_4=1702.67 mg/L)							
BR 2.5	21-May-01	3.55	3.10	731	739	720	648
	15-Aug-01	3.68	3.34	751	737	583	443
	22-Aug-01	3.22	3.01	776	776	1893	1180

Re-measured in February 2003.

Re-measured in April 2002.

Mud Lake exhibits a range of sulphate and iron concentration, and receives neutral clean inflow water. In this lake, some locations had a very low pH in 1996 when the breakthrough of the seepage from the tailings was noted (Table 3d). In the lake pH values as low as 2.5 were measured. When the lake was ice-covered, pH increased as no oxidation of iron could take place. This lake has the highest load of iron particulates and in this data set, unlike those from other water bodies at the SBWMA, there are no samples that do not change to a lower pH.

Table 3d: pH values after storage of cirumneutral surface water in Mud Lake (Re-measured on March 17, 2003)

Samp Date	pH measured:		Eh (mv) measured:		Cond (us/cm) measured:	
	original	re-measured	original	re-measured	original	re-measured
Mud Lake Inflow (Fe=24.7 mg/L; SO_4=34.5 mg/L)						
28-Sep-98	5.53	6.12	426	617	111	83
17-May-00	5.90	6.21	586	563	32	36
Mud Lake at Landing (Fe=55.54 mg/L; SO_4=588.56 mg/L)						
21-Jul-99	2.57	2.53	815	772	1530	1821
Mud Lake at Middle (Fe=99.98 mg/L; SO_4=861.46 mg/L)						
19-May-97	3.57	2.63	582	747	914	1975
30-Aug-97	2.74	2.43	823	809	1580	2250
8-Dec-98	3.30	2.91	662	731	845	1000
14-Mar-99	2.91	2.39	814	748	2600	4820
4-Oct-99	3.25	2.71	678	752	1075	1261
7-Dec-99	3.50	3.08	688	727	633	698
17-May-00	2.85	2.55	774	785	1260	1605
27-Jul-00	2.67	2.44	778	799	1522	1994
1-Feb-03	3.26	2.63	664	776	1416	1514
Mud Lake at Outflow (Fe=82.15 mg/L; SO_4=758 mg/L)						
17-May-00	2.95	2.48	799	787	1020	1724
25-Jun-96	2.52	2.42	734	790	1833	2220
9-Jun-97	2.82	2.35	670	796	1734	2480
7-Dec-99	3.56	2.70	660	773	582	1413
24-Jun-00	3.02	2.96	688	761	660	726
7-Jul-00	2.70	2.50	771	789	1441	1767
1-Feb-01	3.21	2.61	727	784	1385	1462
19-Aug-02	3.19	2.49	771	784	1209	1774
Mud Lake at Outflow Snow Melt (Fe=4.2 mg/L; SO_4=168.0 mg/L)						
10-Mar-00	3.02	3.24	663	724	450	501
10-Mar-00	3.02	3.32	663	780	450	546

However, one interesting observation is the fact that during spring snow melt, both iron and sulphate concentrations are lower at the outflow of Mud Lake, due to dilution. The pH in the stored samples collected at that time increased as did the pH in the stored sample from the clean

water inflow. The lake is very shallow, and at the centre of a large drainage basin turns over three times per year. The inflow water is circum-neutral and also experienced increased pH values in storage.

4. Conclusions

Ecological engineering approaches to the rehabilitation of acid generating wastes allows the natural formation of precipitates and hence the accumulation of sludge or yellowboy.

Generally natural precipitates are considered stable, which is the case as yellowboy ages, and forms the well-defined, secondary mineral goethite. Recent mineralogical research has shed more light on the aging process; original precipitate gradually transforms until it stabilizes as goethite. The geo-microbiological understanding of the process has also progressed however; for geo-microbiologists, considering the multitudes of microbes which derive energy from the transformations, the concept "stable" is practically non-existent.

The data presented from the analysis of samples of tailings pore water and from the various open water bodies in the South Bay Waste Management Area, before, during and after extended periods in storage reflects both the expected mineralogical reactions, expressed by pH depressions, and the buffering capacity of an open system with pH increases. The expected pH depression was never observed, microbes were present and viable.

The concern that Schwertmannite formation would lead to acidification is likely a consideration of only theoretical importance; for all practical purposes it will not be detrimental to the proposed approach. The instability of the precipitate and the activity of the microbes may well reflect the natural equilibrium expected from homeostasis. However, to bring as much certainty as possible to the Ecological Engineering approach at South Bay, which integrates the natural formation of yellowboy in the BRC ditch, samples have been submitted for mineralogical analysis.

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Second Sample Shipment to B. Johnson	3	T:\Yan\South Bay\Tailings\Paper SchwermaniteAppendix\Microbial results\second results July 2002.pdf
Water chemistry and elemental concentration at M27C, M27S, M7N, M7S	4	T:\Yan\South Bay\Tailings\Paper SchwermaniteAppendix\Microbial results\M27C 27S 7N 7S chemistry.xls
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Estimation of long-term pyrite oxidation rates in above ground base metal tailings deposits	10	T:\Yan\South Bay\Tailings\Paper Schwermanite\Appendix\Gerits report\oxidation rates 1\oxdication rate.doc, oxidation rate tab1-2.xls, oxidation rate tab3.doc
Total of 35 slides of particles on filter papers from ground and surface waters	D	Paper copy only
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